Cu-Zn BINARY PHASE DIAGRAM AND DIFFUSION COUPLES

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KEY WORDS: Phase diagram, diffusion, diffusion couple, diffusion rate.

PREREQUISITE KNOWLEDGE: This experiment could be performed by students taking an introductory-level materials science course.

OBJECTIVES:
1. To learn what information a binary phase diagram can yield.
2. To learn how to construct and heat treat a simple diffusion couple.
3. To learn how to prepare a metallographic sample.
4. To learn how to operate a metallograph.
5. To learn how to correlate phases found in the diffusion couple with phases predicted by the phase diagram.
6. To learn how diffusion couples held at various temperatures could be used to construct a phase diagram.
7. To learn the relation between the thickness of an intermetallic phase layer and the diffusion time.
8. To learn the effect of one species of atoms diffusing faster than another species in a diffusion couple.

EQUIPMENT AND SUPPLIES:
1. Three copper rods (99.9+% purity), about 1.27 cm (0.5 inch) in diameter and 4 to 5 cm in length.
2. About 400g of mossy zinc (99+% purity).
3. Three Pyrex test tubes, about 2.5 cm in diameter and 20 cm in length.
4. One stainless steel test tube holder.
5. One ceramic crucible, at least 200 ml capacity.
6. Appropriate safety equipment such as a face shield, heat-resistant gloves, and tongs to handle the crucible and test tubes containing 600°C molten zinc.
7. One furnace capable of maintaining 600°C and with a chamber at least 21 cm tall.
8. Standard metallographic sample preparation equipment.
9. Etchant consisting of 20 ml NH_4OH, 40 ml water, and 5 ml H_2O_2 (3%).
10. Light metallograph with a Polaroid camera attached.

PROCEDURE:

1. Weigh out 400g of mossy zinc and place it in the ceramic crucible.*
2. Place the crucible in a 600°C furnance and hold for about a half-hour until all the zinc is molten.
3. Clean the surfaces of the three copper rods using 120 grit paper.
4. Center one copper rod in the bottom of each test tube.
5. Place the test tube holder containing the three test tubes with the copper rods in the same furnace as the crucible for about 5 minutes to preheat the copper and to ensure the dryness of the copper and the glass.
6. Carefully remove both the crucible and the test tube rack from the furnace using the appropriate gloves, face shield, and tongs. Reset the furnace to 400°C.
7. Quickly skim aside the oxide residue floating on the molten zinc and pour the zinc in equal proportions into each test tube to about 6 cm of height, completely covering the copper rods with molten Zn.
8. Immediately return the test tube rack containing the samples to the furnace (now set at 400°C).
9. After holding at 400°C for 1 day, 4 days, and 9 days respectively, remove each sample from the furnace and quench in water. Be careful as the glass tube will crack as it is quenching.
10. Engrave identifying codes on the top and bottom parts of each diffusion couple.
11. Using a cutoff wheel or saw, cut transversely each diffusion couple in half.
12. Prepare metallographically the cut surface of one of the two halves of each diffusion couple, starting with 120-grit paper and working progressively through a 1-µm abrasive polish.
13. Etch the polished surfaces using the etchant described in the previous section. When mixing and applying the etchant, use gloves and eye protection. It will take only a few seconds of swabbing this etchant on the sample to etch it, as seen by the zinc portion of the diffusion couple turning a gray color.
14. View each sample under the light metallograph at magnifications varying from 50x to 500x. Find regions where there are no gaps between the Zn jacket and the Cu core. Identify the β, γ, and ϵ phase layers in each of the three diffusion couples and take Polaroid photos at 50x similar to those shown in Figure 1.
15. In order to more easily measure the width of the relatively narrow β-layer, additional photos at 500x should be taken of each of the diffusion couples (see Figure 2).
16. From the photos, measure the average width of β and γ layers for each diffusion couple as shown in Table 1. Find a simple mathematical relationship between the layer width versus the diffusion time for both the β and γ layers.
17. Observe the location of the phase layers relative to the original Cu-Zn interface.
18. Observe the location of holes or voids in the microstructure of the diffusion couples.

* Add flux if desired.

112

SAMPLE DATA SHEETS:

TABLE 1.   INTERMETALLIC PHASE LAYER WIDTHS

Time (days)	β-layer width (mm) (from photos at 500x)	Ratio of β-layer width to width at 1 day	γ-layer width (mm) (from photos at 50x)	Ratio of γ-layer width to width at 1 day
1	2.7	1	25	1
4	4.9	1.8	52	2.1
9	7.6	2.8	70	2.8

INSTRUCTOR NOTES: The instructor should provide each student with a copy of the Cu-Zn phase diagram. Across the phase diagram at 400°C, the student should draw a horizontal line (as shown in Figure 3) to determine the chemical composition (wt. % Zn) of each phase at the various phase interfaces. These chemical compositions indicate the solubility limits of Zn in each phase. Emphasize that the layers of intermetallic phases seen in the diffusion couples should have composition ranges predicted by the phase diagram at 400°C and not at room temperature since the water quench locks in the 400°C microstructure. Figure 3 is also useful to explain how diffusion couple experiments could be used to construct a phase diagram. Several diffusion couples of the same two metals could be held at different temperatures for a period of time, quenched, and then analyzed as to the chemical composition of the phases at the layer interfaces. After collecting the solubility limits of the phases at the different temperatures, the phase diagram could be constructed.

An approximate composition profile of the diffusion couple, as shown in Figure 4, is easy to construct from the information obtained from Figure 3 if one assumes that the chemical composition varies linearly as one moves across each single phase region. Together, Figures 3 and 4 are helpful in explaining why the chemical composition changes abruptly across each phase interface as well as why there are no regions consisting of a mixture of two phases in the diffusion couple even though such regions appear to exist in the phase diagram.

Depending upon the student level, the instructor could explain how Fick's Second Law of Diffusion predicts that the width of each phase layer varies with the square root of the diffusion time when the diffusion temperature is held constant. This relationship is easy for the student to deduce when using the diffusion times of 1 day, 4 days, and 9 days since the relative thickness of a particular layer is found to be approximately in a simple 1:2:3 ratio as shown in Table 1.

The student should be informed that the Zn atom diffuses much faster than the Cu atom. This fact can be used to explain why the intermetallic phases all form on the Cu side of the original Cu-Zn interface. It also can explain the formation of voids in the γ and ε phases since the Zn atoms are moving in toward the center of the couple faster than Cu atoms are moving out toward the Zn jacket. This phenomenon is called the Kirkendall effect.

One of many applications of the principles learned from this experiment involves the manufacturing process to form wire of the superconductor Nb_3Sn (see page 604 of reference 1). In this process, a composite consisting of niobium wire imbedded in a copper matrix is plated with tin. When heated, the tin diffuses through the copper and reacts with the niobium to produce the Nb_3Sn superconductor in the form of wire.

Another application of diffusion principles involves the carburizing of steel to form a hard, high-carbon case around a softer, low-carbon core (see pages 386-387 of reference 2). If the amount of carbon present at the surface of the steel and the carburizing temperature are both held constant, then the depth of the resulting hardened case is found to vary as the square root of the carburizing time.

Still another application is the explanation of a premature failure of integrated circuits called the "purple plague" (see page 133 of reference 2). It is called the "purple plague" because of the surface discoloration that accompanies the failure. This failure occurs at the interface where gold wire leads are welded to aluminum terminals of the integrated circuit. During the operation of the integrated circuit, the Al atoms diffuse faster across the interface than the Au atoms. The resulting formation of voids at this interface due to the Kirkendall effect can eventually cause the electrical connection to fail.

REFERENCES:
1. D.R. Askeland, The Science and Engineering of Materials, 2nd Edition, PWS-Kent Publishing Co., 1989, pp. 131-133, 385-387, 604.

2. F.N. Rhines, Phase Diagrams in Metallurgy, McGraw-Hill Book Co., 1956, pp. 107-109.

SOURCE OF SUPPLIES:
The mossy zinc can be readily obtained from most any chemical supply company for less than $25 for a 1-kg jar. To buy the copper rod, contact your local metal supply house. A standard mill-size rod 12 feet long and 1/2-inch diameter of 99.9+% copper should cost about $50.

Figure 1. Single-phase layers in the Cu-Zn diffusion couples held at 400° C
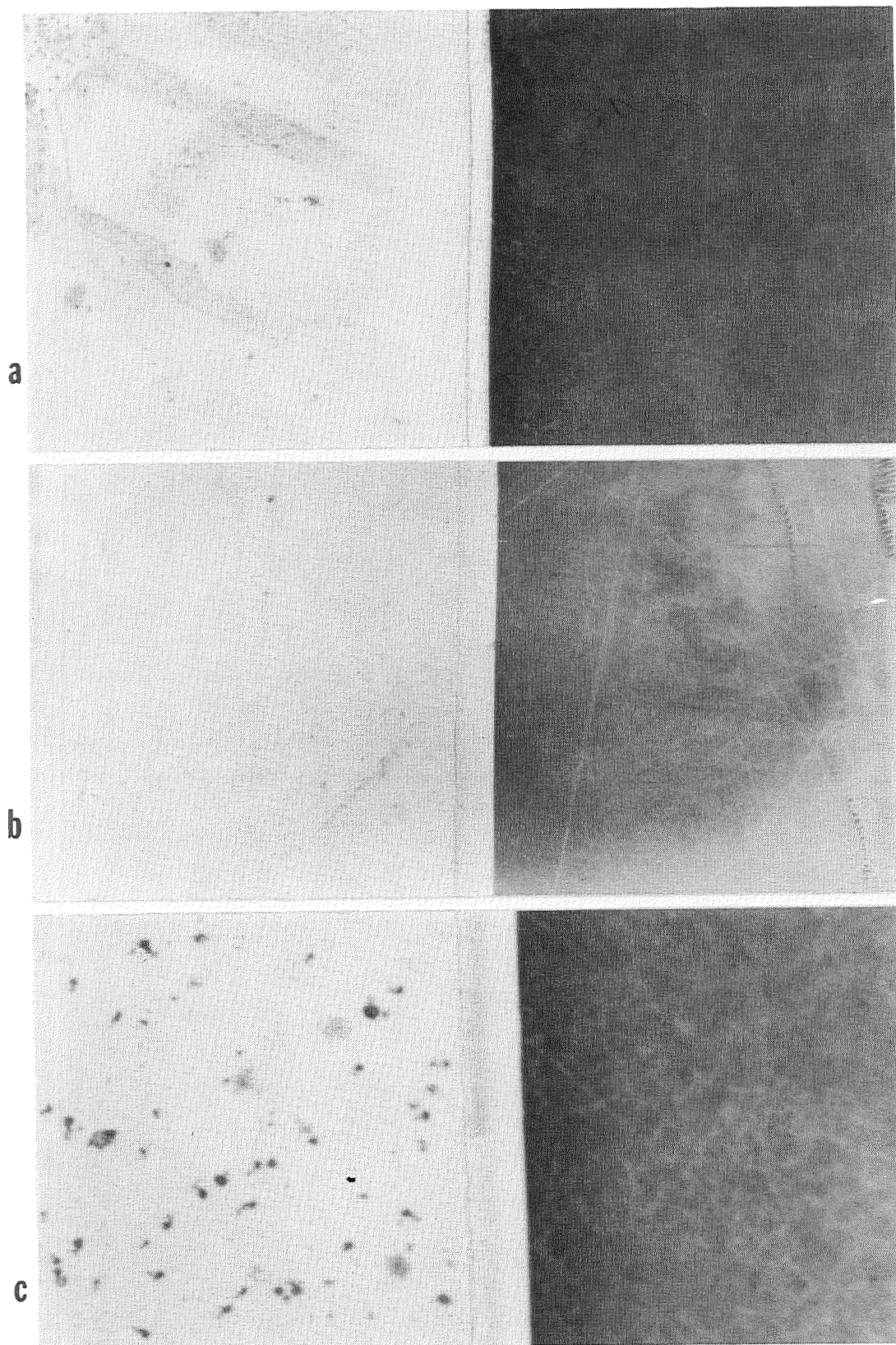for (a) 1 day, (b) 4 days, (c) 9 days. Mag. 50x.

Figure 2.   Growth of the β-layer in the Cu-Zn diffusion couples held at
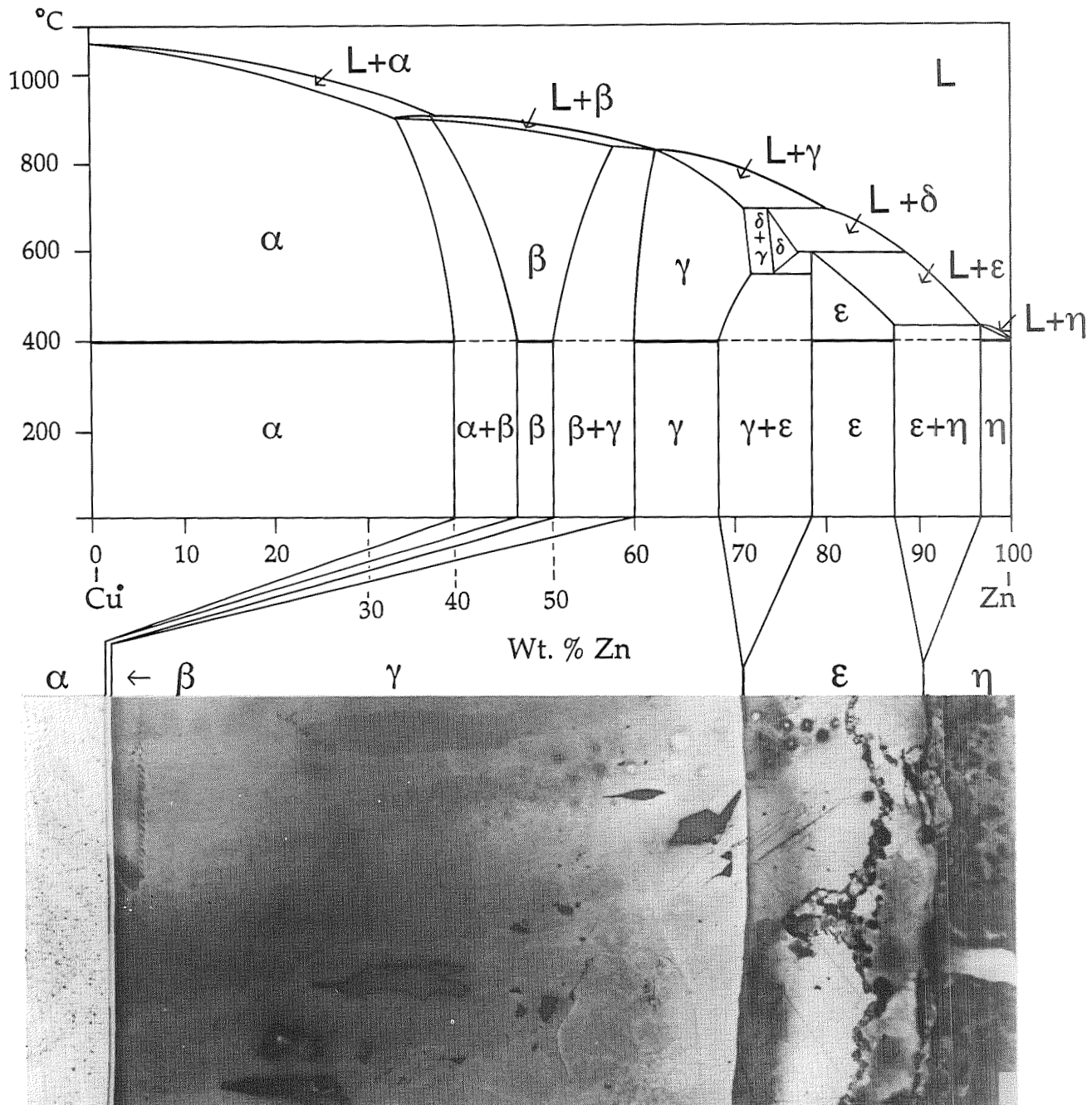400⁰C for (a) 1 days, (b) 4 days, (c) 9 days. Mag. 500x.

116

Figure 3. Correlation between the Cu-Zn phase diagram showing equilibrium phases at 400° C and the single-phase layers formed in the Cu-Zn diffusion held at 400° C for 9 days. Adapted from page 108 of reference 1.
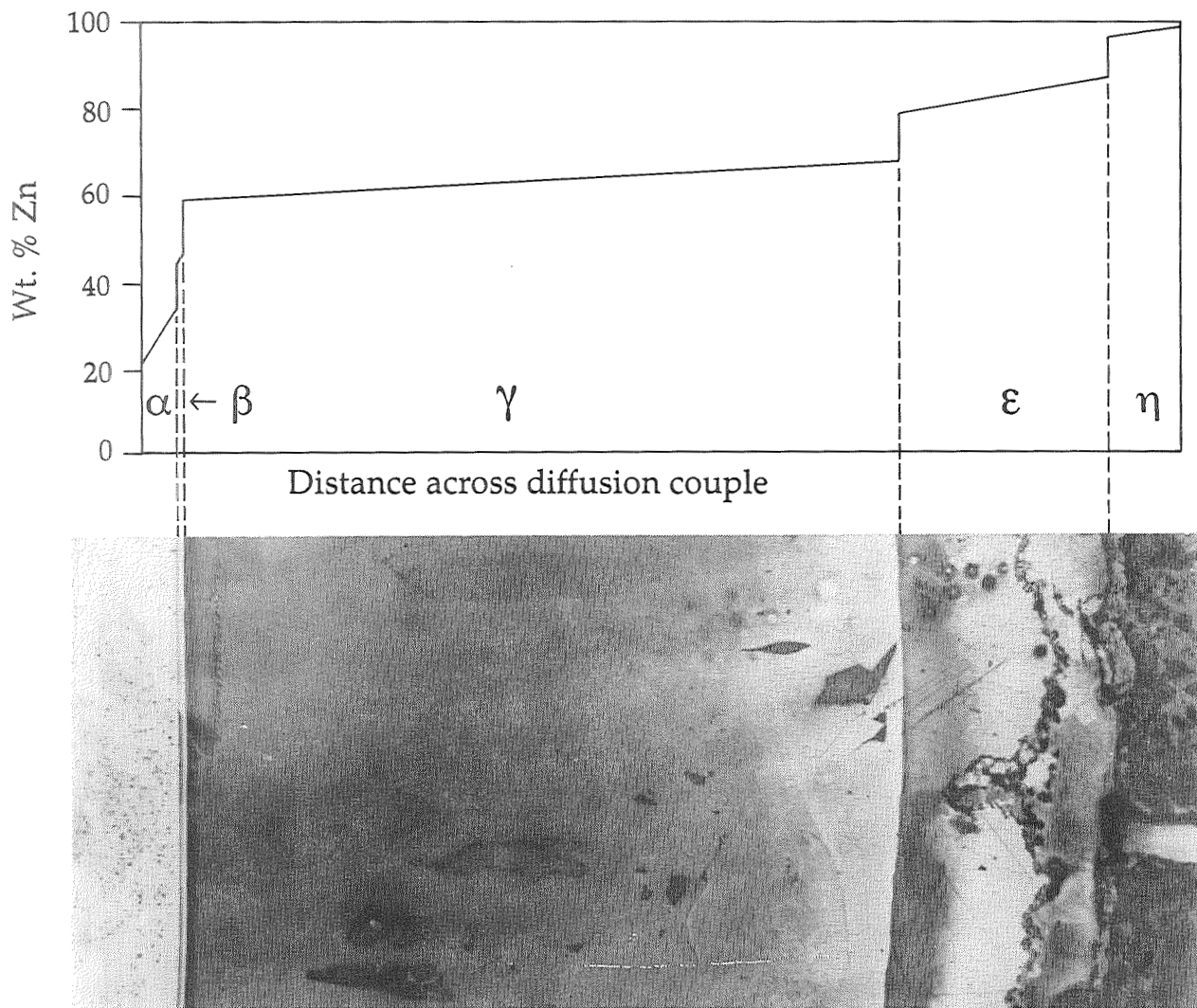
117

Figure 4. Composition profile of the Cu-Zn diffusion couple held at 400°C for 9 days.